ACCURATE DETERMINATION OF THE MAGNETIC ANISOTROPIES OF THE HYDRATED SALTS OF SOME ELEMENTS OF THE IRON GROUP

By SUNILKUMAR DATTA

Department of General Physics, X-Rays and Magnetism, Indian Association for the Cultivation of Science, Calcutta—32

(*Received for publication, April 24, 1954*)

ABSTRACT. Van Vleck's recent theory of magnetic anisotropy of paramagnetic crystals indicate the importance of the effects of long range crystalline electric fields which were previously assumed to be small in comparison with short range ones. Experimental verification of this theory necessitates very accurate determination of the magnetic anisotropy of such crystals. This has been undertaken in the present work in which attempts have been made to improve the existing methods in order to eliminate or minimise errors that arise in its measurement, especially in the control and measurement of the magnetic field. The results obtained on a large number of crystals show considerable differences from those obtained by the previous workers. The use of single crystals as secondary standards in the measurement of magnetic fields has been discussed.

1. INTRODUCTION

The most extensive measurement of the magnetic anisotropies of the single crystals of paramagnetic salts has been done by Krishnan and his co-workers in this laboratory (1933, *et seq.*) with the intention of verifying and elucidating many important aspects of the crystalline electric field theory of Van Vleck (1932) and Penney and Schlapp (1932). Some of their earlier works were, however, found to be largely in error; for example, the principal gram molecular anisotropy of $NiSO_4, 6H_2O$ was found to be 83.0×10^{-6} at 303°K by Mookerjee (1946) and 81.6×10^{-6} at 303°K by Stout and Grieffel (1950), as against 109×10^{-6} by Krishnan *et al* (1933). Joglekar (1938) also found for some of the ammonium Tutton salts a difference of even 8% from the anisotropies given by the earlier workers. The 'oscillation method' used by the earlier workers was not evidently very reliable. Even in the later works following the 'critical couple method' the over-all experimental accuracy perhaps never exceeded 1 to 3%, the main uncertainty lying in the field stabilization and measurement, crystal purity and perfection and accurate torsion determinations.

According to Van Vleck's later theory (1939) the direct and the indirect effects,—particularly the latter,—of the long range asymmetric crystalline electric fields on the paramagnetic ions are not negligible in comparison with with the short range ones. In fact, the indirect effect may be sometimes

comparable with and even predominant to that of the latter, and in general these two effects are superimposed to give the total asymmetry of the Jahn Teller clusters (1937) about the paramagnetic ions. For a given paramagnetic ion the effect of the asymmetric long range fields should vary from salt to salt and to detect such an effect accurate values of the magnetic anisotropies and their temperature variations would be most useful. In view of this the present redeterminations have been undertaken to improve the accuracy to 0.1% or better of the anisotropies of a large number of salts. A number of new salts, interesting from magnetic and structural view point, not previously measured are also included. Temperature variation measurements over a wide range are nearing completion and theoretical discussions of the present results are left over till then.

2. IMPROVEMENTS IN THE EXPERIMENTAL METHODS

The principle of the method for anisotropy measurement is the same as in the later works of Krishnan *et al* and need not be described in detail. It depends on the measurement of the critical torsion angle of a fine quartz fibre, attached at the upper end to a torsion head and with the crystal at the lower end placed in a homogeneous horizontal magnetic field H. In the position of unstable equilibrium of the crystal under the opposing couples due to the fibre and the field the condition is given by

$$\Delta\chi = \frac{\alpha_c - \pi/4 - \sigma_c}{\cos 2\sigma_c} \times \frac{2MC}{mH^2}$$

where $\sin 2\sigma_c = MC/mH^2\Delta\chi$, $\Delta\chi$ the magnetic anisotropy of the crystal in the horizontal plane, M is the gm molecular weight of the crystal of mass m and C is the torsion constant of the quartz fibre.

The values of M are obtained from the International Critical Tables on the basis of the molecular formula of the salts, which might differ appreciably from the stoichiometric proportions of the containing elements only in the case of imperfect crystals containing sufficient occlusions of mother liquor or other impurities. Such cases were summarily rejected. The salts taken were always of the analytical qualities of Kahlbaum, E. Merck (of these two we had some pre-war stock in our laboratory) or Malinckrodt or B. D. H., or else prepared by ourselves from such analytical quality starting materials (*e.g.*, the fluo-salts). The salts were recrystallized twice or thrice using double distilled water and were always tested for the final purity. The final crystallization was done in a quiet, dust free and vibration-proof chamber, by moderately slow evaporation of a nearly saturated aqueous solution. It was unfortunate that our resources did not allow us to have an air-conditioned room. The best of the crystals were chosen first with a magnifying glass and then under a petrographic microscope. Finally, goniometric measurement was done as test cases which agreed very well with the standard data for these salts.

The mass of the crystal varied between 0.1 and 0.05 gm and was determined accurately to 0.1% or better with a calibrated Bungé balance giving a direct rider reading to 0.1 mgm and by oscillation to 0.03 mgm The weights were corrected for buoyancy of air. The method of accurately determining C, the torsion contant of the quartz fibre has been discussed in a previous paper by the author (1953), the accuracy of which is 0.1% or better.

3. CONTROL AND MEASUREMENT OF THE MAGNETIC FIELD

As equation (1) involves the square of the field H, much improvement upon the usual method is called for to arrive at an accuracy of about 0.05% in its measurement. The value of the residual field and the initial state of magnetization of the magnet core and the pole pieces decide to a large extent the final total field when the magnetizing current is established. To arrive at a steady initial condition of the magnet for a given final magnetizing current a reversing switch with a rheostat is arranged in the magnet circuit and the core and pole pieces are subjected to several hysteresis cycles before the final current is established. The current for the magnet was taken from a special 10 kW 220 V d.c. compound wound generator on which no other load was allowed during these measurements. The huge self-inductance of the magnet was by itself a stabilizing factor. The current was read on a calibrated 5″ mirror-dial Weston ammeter of 5 ampere range, the fine needle of which touching a desired scale-division was observed against the cross-wires of a low power microscope. Fluctuations of the current could thus be easily detected to 0.5 milliamperes, *i.e.*, 0.01% in 5 amperes. No low frequency fluctuations were observed by us. But very slow drifts by about 10 milliamperes occurred over 8 to 10 minutes, perhaps due to heating of the circuit and other causes. More troublesome were sudden kicks by about 0.1 ampere, probably due to fluctuations in the 440 a.c. mains. If such a kick occurred at the moment when the crystal to be measured has been rotated nearly to the unstable position in the field, very often the result was to make the crystal spin round prematurely. The result of such an observation was forthwith rejected. Otherwise all variations in the current were controlled to a nicety with the help of a fine-wire screw motion sliding contact rheostat placed in the circuit. Particular check on the exact value of the current was kept near the unstable position.

Before the actual measurement of the field was carried out the unformity of the field over the central region of the pole-gap was checked. The pole-gap was 4 cm between 10 cm × 10 cm flat non-tapered pole pieces made parallel accurately to 1/1000 mm. The exciting current was 4 amperes. The method was to measure the critical couple on a very well-developed crystal of $CuSO_4$, $5H_2O$, about 4mm × 3 mm × 2 mm (the anisotropy $\Delta\chi$ with the c axis vertical, as measured by Krishnan and Mookerjee (1938) to be

observing the crystal through a telescope arrangement described later. But small additional uncertainties may arise in both the initial and final positions due to residual field, anisotropy of shape of the crystal, eccentricities of mounting of the crystal and the torsion head, etc. Elimination of the anisotropy of shape is discussed in a later section whilst the others are eliminated completely by taking the mean of the clockwise and anticlockwise rotations of the torsion head. The final position is also very much dependent upon the fluctuations in the magnet field (also discussed later), quick and yet smooth operation of the torsion head during measurement, etc. A moderate rotation of the torsion head by two revolutions, say, could be smoothly given in about a minute without making the crystal oscillate much near the critical position. Actually, several readings never differed by more than 0.1% and their mean was taken. σ_θ is a small correction term for large angles of torsion and is less than 0.1% above 680°. For smaller angles it becomes appreciable and can be readily calculated with a sufficient degree of accuracy for our purpose.

6. ANISOTROPY OF SHAPE AND ITS ELIMINATION

The anisotropy of shape in crystals of representative members of the Tutton salts was estimated by grinding out thin plates measuring about 10mm × 6mm × 1mm and determining their anisotropy in air and again in a balancing bath of the same mean susceptibility, following the method of Krishnan, *et al* (1933) for determining the anisotropy of Mn^{++} and Fe^{+++} salts. For cobalt, iron and copper salts the anisotropy of shape even with such high asymmetry of shape was found to be less than 0.1%, whereas for nickel salts it amounted to a few parts in a thousand, of the true magnetic anisotropy of the crystal. For example, a $NiSO_4, 6H_2O$ crystal, about (12mm × 12mm) × 1mm thick had an anisotropy of 81.3×10^{-6} in air and 80.8×10^{-6} in the balancing bath. Our actual crystals were chosen to have developments to comparable extent on all sides as far as possible to minimise this effect. However, in such cases as above balancing baths were always used in subsequent measurements. To use crystals in the form of discs would be a good procedure for many purposes, but for the present we avoided it in order to minimise (*a*) errors in locating the axes of the crystal and hence measuring the orientation of the crystal in the field directly and (*b*) chances of contamination, both of which may be considerable.

7. MEASUREMENT OF θ AND ψ

For monoclinic crystals in addition to the principal anisotropies the angles between the crystallographic *a* axis and the maguetic χ_2 axis and that between *c* and χ_1 axis denoted by θ and ψ respectively which are connected by

the relation $\theta+\psi+\pi/_2=\beta$ according to the notations adopted by Krishnan, was also measured in an improved manner than the earlier workers, as follows. A $NiSO_4$, $6H_2O$ crystal belonging to the tetragonal system with large well-developed c (001) face was mounted with the tetrad axis horizontal, and the torsion head adjusted till the crystal was under no torsion in the field. This position can be obtained without much difficulty to within 0.1° taking into consideration the slight uncertainty due to the residual field and the limitations of the reading of the vernier torsion head. The lamp and telescope, previously arranged to view the crystal horizontally approximately normal to the direction of the field, was then adjusted so as to get the image of the filament of the lamp over the cross wire, being reflected by the c face of the crystal which set itself along the field. The orientation of any vertical face with respect to the field, of any other crystal also, could then be determined quite easily. For example, in a monoclinic crystal suspended with the b axis vertical the angle between the χ_1 and a axis (that is $90-\theta$) was directly determined in magnitude with an accuracy of 0.1°. The sign of θ was determined by noting the position of any other (hol) plane with respect to the χ_1 direction, since according to conventions θ (or ψ) is taken as positive when it lies within the monoclinic angle β, otherwise negative. ψ was then calculated from the previous relation or measured directly if the crystal had suitably developed faces.

For monoclinic crystals the three usual modes of suspension were used :

(*i*) b axis vertical, giving

$$\Delta\chi=\chi_1-\chi_2 \tag{2}$$

(*ii*) a axis vertical, giving

$$\Delta\chi=\pm\{(\chi_1-\chi_2)\sin^2\theta-(\chi_1-\chi_3)\} \tag{3}$$

and (*iii*) (001) plane horizontal, giving

$$\Delta\chi=\pm\{(\chi_1-\chi_2)\cos^2\theta-(\chi_1-\chi_3)\} \tag{4}$$

the + ve or − ve sign being chosen according as the (b) axis lies normal or along the field.

For orthorhombic crystals suspensions along the principal diad axes a, b, c were used whilst for tetragonal or trigonal crystals the tetrad or the triad axes were suspended horizontally.

The data recorded below represent in all cases the mean value for at least five crystals agreeing with each other to within 0.3 to 0.1% or better. The temperature of measurement varied from about 25° to 30°C but they have been converted to 300°K from the slopes at this point of the temperature-anisotropy curves of Bose (1945), Guha (1951) or from author's own measurements to be published elsewhere.

TABLE I

Magnetic anisotropy ($\times 10^{-6}$) of crystals at 300°K. Figures within parentheses denote the values obtained by the previous workers referred to against them.

Crystal	Crystal class	$\chi_1-\chi_2$	$\chi_1-\chi_3$	$\theta°$	$\psi°$	Reference
1. $K_2Fe(SO_4)_2, 6H_2O$	Monoclinic	1696 (1841)	−279.6 (−314)	−43.4 (−43 8)	+57.9 (+58.3)	1
2. $(NH_4)_2Fe(SO_4)_2, 6H_2O$	,,	2179 (2582)	180.1 (213)	−37.4 (−37)	+53.4 (+54)	1
3. $FeSO_4, 7H_2O$	,,	1166 (1289)	1143 (1270)	−8.1 (−7.5)	+22.4 (+22)	1
4. $K_2Co(SO_4)_2, 6H_2O$	,,	2432 (2532)	1772 (1832)	+30 5 (+30 5)	−15 6 (−15 5)	1
5. $(NH_4)_2Co(SO_4)_2, 6H_2O$	,,	3042 (3023)	1543 (1541)	+60.2 (+60)	−43.3 (−43)	1
6 $CoSO_4, 7H_2O$	,,	1823 (1928)	956 (1094)	+68.6 (+69 1)	−54.6 (−54.4)	1
7. $K_2Ni(SO_4)_2, 6H_2O$	,,	131.2 (158)	130.5 (165)	+26.7 (+27)	−11.4 (−12)	1
8. $(NH_4)_2Ni(SO_4)_2, 6H_2O$	,,	93.8 (110)	91.5 (106)	+31.0 (+31)	−13.4 (−14)	1
9 $Rb_2Ni(SO_4)_2, 6H_2O$	,,	143.3 (144)	136 8 (137)	+27.5 (+27.0)	−11.4 (−11.0)	2
10. $Tl_2Ni(SO_4)_2, 6H_2O$	,,	113 7 (114)	107 4 (108)	+26.5 (+27 3)	−10 1 (−20.9)	2
11. $Cs_2Ni(SO_4)_2, 6H_2O$	,,	132.2 (134)	126.1 (127)	+27.1 (+27.7)	−10.1 (−10.7)	2
12. $NiSO_4, 7H_2O$	Orthorhomic	$\chi_a-\chi_b=159.6$ (169) (163)		$\chi_a-\chi_c=31\ 9$ (49) (35)		1 4
13. $NiSO_4, 6H_2O$	Tetragonal	$\chi_1-\chi_{11}=80.8$ (109) (83) (81.6)				1 4 6
14. $K_2Ni(SeO_4)_9, 6H_2O$	Monoclinic	127 3 (146)	107.2 (146)	+31 0 (+27.5)	−16.5 (−13 0)	2
15. $(NH_4)_2Ni(SeO_4)_2, 6H_2O$	,,	92.6 (116)	79 6 (96)	+38.1 (+44 2)	−22.1 (−27.9)	2
16. $Rb_2Ni(SeO_4)_2, 6H_2O$	,,	136.5 (157)	117.0 (147)	+28.0 (+28.2)	−12.7 (−12 9)	2
17. $Tl_2Ni(SeO_4)_2, 6H_2O$	,,	122.5 (123)	116 5 (118)	+32.7 (+32.7)	−17.1 (−17.1)	2
18. $Cs_2Ni(SeO_4)_2, 6H_2O$	,,	131.5 (164)	110 7 (135)	+28 5 (+33.8)	−11.3 (−17 6)	2
19. $NiSeO_4, 6H_2O$	Tetragonal	$\chi_1-\chi_{11}=$	86 6 (90)			2

TABLE I—contd

Crystal	Crystal class	$\chi_1-\chi_2$	$\chi_1-\chi_3$	$\theta°$	$\psi°$	Reference
20. $K_2Ni(BeF_4)_2, 6H_2O$	Monoclinic	132 1	128.5	+28.5	−13.4	
21 $(NH_4)_2Ni(BeF_4)_2, 6H_2O$	,,	105 8 (107)	101.1 (106)	+29.2 (+31.0)	−12 5 (−14 3)	2
22. $Rb_2Ni(BeF_4)_2, 6H_2O$	,,	122.3	118.4	+27.1	−10.8	
23 $Tl_2Ni(BeF_4)_2, 6H_2O$	,,	121.0	117.9	+26.9	−11.1	
24. $Cs_2Ni(BeF_4)_2, 6H_2O$	,,	117.3	115.2	+26 2	−9 1	
25. $NiSiF_6, 6H_2O$	Trigonal	$\chi_{\parallel}-\chi_{\perp}=$	18.18			
26 $K_2Cu(SO_4)_2, 6H_2O$	Monoclinic	322 3 (367)	72 4 (74)	−88.1 (−88)	−77.4 (−77 5)	1
27 $(NH_4)_2Cu(SO_4)_2, 6H_2O$	,,	285.7 (300)	67.6 (62)	−60.1 (−61)	+75.0 (+77)	1
28. $Rb_2Cu(SO_4)_2, 6H_2O$	,,	329.7 (350)	94.2 (100)	+84.7 (+86.1)	−69. (−704.0)	2
29. $Tl_2Cu(SO_4)_2, 6H_2O$	,,	302.5 (283)	84 9 (71)	+88.5 (+88 2)	−72.1 (−72.6)	2
30 $Cs_2Cu(SO_4)_2, 6H_2O$	,,	329 7 (339)	111.2 (114)	+87 9 (+88.1)	−71.8 (−71 9)	2
31. $K_2Cu(SeO_4)_2$ $6H_2O$	,,	340 3 (367)	111.8 (95)	−61 5 (+66.9)	+74.9 (−53.5)	2
32 $(NH_4)_2Cu(SeO_4)_2, 6H_2O$	,,	322 6 (353)	111.6 (118)	−52 1 (−51.2)	+68.0 (+66.7)	2
33. $Rb_2Cu(SeO_4)_2, 6H_2O$	,,	326 3 (354)	77 1 (78)	−86.5 (+88.0)	−78.8 (−73-3)	2
34. $Tl_2Cu(SeO_4)_2$ $6H_2O$	,,	305 1 (328)	71 3 (22)	−87.5 (+87 3)	−77.6 (−72 3)	2
35. $K_2CuCl_4, 2H_2O$	Tetragonal	$\chi_1-\chi_{\parallel}=$	260.1 (268) (263)			3 5
36 $(NH_4)_2CuCl_4, 2H_2O$	,,	,,	255.3 (260) (258)			3 5
37. Rb_2CuCl_4 $2H_2O$	,,	,,	254 6 (265) (262)			3 5
38. $(NH_4)_2CuBr_4, 2H_2O$	,,	,,	235.5			

References: 1. Krishnan, Chākravorty and Banerjee (1933), 2. Krishnan and Mookerjee (1938), 3. Krishnan, Mookerjee and Bose (1939), 4. Mookerjee (1946), 5. Mookerjee (1945), 6. Stout and Grieffel (1950).

8 DISCUSSIONS

Without going into theoretical interpretation of the above data at present, several points of interest relating to them may be mentioned. A glance at the table will show that the values of anisotropy obtained by the present author are considerably at variance with those of Krishnan, Chakravorty and Banerjee (1933) whose values for iron, nickel and copper salts are upto 20% higher in some cases. This may possibly be due to the "oscillation" method being not sufficiently accurate. The values given by Krishnan and Mookerjee (1938) are more near to the present values, though almost systematically high by a few per cent. This might arise due to their value of magnetic field being slightly in error (about 1.5 to 2%) on the negative side. The values of θ and ψ, however, in all cases agree quite closely with the previous values, except in the case of $K_2Cu(SeO_4)_26H_2O$ for which the previous workers gave: $\theta = +66.9°$ and $\psi = -54.5°$, as against those of the present author: $\theta = -61.5°$ and $\psi = +74.9°$. Obviously, the difference in sign in the two values of θ is of significance and explains the discrepency pointed out by Bleaney *et al* (1949) between the value of ψ obtained by Krishnan and that from their own paramagnetic resonance experiments, namely $+73°$. The present author's value is in agreement with that of Bleaney.

It has been one of the objects of our researches in this laboratory to use the present method for the determination of field strength using a suitable crystal of accurately known anisotropy. The great advantage of this method (which is, of course, restricted to homogeneous horizontal fields) lies in its extreme simplicity and accuracy. On account of the smallness of the size of the crystal in comparison with the search coil it may conveniently be used even in very narrow spaces within the pole-gap; different parts of the field may also be explored, as has been done in the present measurements. Crystals of $CuSO_4, 5H_2O$ have hitherto been used in this laboratory and elsewhere (*cf.* Selwood, 1950) for this purpose; these crystals sometimes contain occlusions in the form of bluish white patches, possibly of a basic composition. Moreover, they do not give reproducible values of anisotropy after storage for a few months. On the other hand, $NiSO_4, K_2SO_4, 6H_2O$ crystallizes very well and is practically free from occlusions, flaw or strain, as revealed from their optical examination, and gives reproducible values even after long storage. These crystals are also magnetically quite stable, that is, the change in θ and ψ are quite small over a wide range of temperatures. These properties make the substance very suitable for measuring magnetic fields.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. A. Bose, D.Sc., for kind help and keen interest in connection with this work.

REFERENCES

Bleaney, B., Penrose, P, and Plumpton, B. P., 1949, *Proc. Roy. Soc.* **A198**, 406
Bose, A. 1947, *Ind. J. Phys.* **21**, 275;
,, 1948, ,, ,, ,, **22**, 73, 195, 275, 483.
Bose, A. and Mitra, S. C., 1952, *Ind. J. Phys.*, **26**, 393, 543.
,, ,, 1953, ,, ,, ,, **27**, 95.
,, ,, 1954, *Proc. Roy. Soc.*, (In course of publication).
Datta, S., 1953, *Ind. J. Phys.* **27**, 155.
Dutta Roy, S., 1954, *Ind. J. Phys.* **28**, (In course of publication).
Guha, B. C., 1951, *Proc. Roy. Soc.*, **206**, 355
Hahn, H. and Teller, E., 1937, *Proc. Roy. Soc.* **A161**, 220.
Joglekar, M. S., 1938, *Z. Krist.* **98**, 411.
Krishnan, K. S., Chakravorty, N. C., and Banerjee, S., 1933, *Phil. Trans. Roy. Soc.*, **A232**, 99.
,, and Mookerjee, A., 1938, *Phil. Trans. Roy. Soc.*, **A237**, 99
,, ,, 1938, *Phys. Rev.*, **54**, 533, 841.
Mookerjee, A., 1945, *Ind. J. Phys.*, **19**, 63.
Mookerjee, A. 1946, *Ind. J. Phys.*, **20**, 9.
Penney, W. G., and Schlapp, R., 1932, *Phys. Rev.*, **42**, 666.
Selwood, P. W., 1952, *J. Amer. Chem. Soc.*, **74**, 2364.
Stout, J. W., and Grieffel, M. 1950, *J. Chem. Phys.*, **18**, 1449.
Van Vleck, J. H., 1932, Theory of Electric and Magnetic Susceptibilities, (Oxford)
,, 1932, *Phys. Rev.*, **41**, 208.
,, 1939, *J. Chem. Phys.*, **7**, 61